

1,2,3,4,4a,12a-Hexahydro-2,5,5-trimethyl-1H-[2]benzopyrano[3,2-c]coumarin

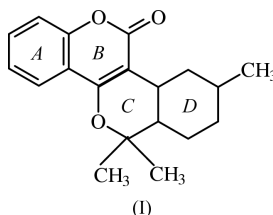
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Key indicators

Single-crystal X-ray study
T = 293 K
Mean $\sigma(\text{C}-\text{C}) = 0.003 \text{ \AA}$
R factor = 0.042
wR factor = 0.114
Data-to-parameter ratio = 11.3For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.The dihydropyran ring in the title compound, $\text{C}_{19}\text{H}_{22}\text{O}_3$, adopts a half-chair conformation and the cyclohexane ring is in a chair conformation. In addition to van der Waals interactions, the molecular packing in the crystal is stabilized by $\text{C}-\text{H}\cdots\pi$ interactions, involving the dihydropyran ring of the symmetry-related molecules.

Comment

Coumarin derivatives possess a variety of biological activities (Crombic *et al.*, 1985). They are used in oral anticoagulation therapy (Cole *et al.*, 1988; Greenfield, 1988) and in enzyme inhibitors (Michel & Durant, 1976). Coumarin derivatives exhibit solid-state photochemical reactions (Gnanaguru *et al.*, 1985). Some amino- and hydroxycoumarin derivatives are used as laser dyes (Masilamani, 1979). As part of our studies on these derivatives, the X-ray structure determination of the title compound, (I), was undertaken.

The title molecule (Fig. 1) contains a fused four-ring system *A/B/C/D*. The geometry of the coumarin ring system (Table 1) is comparable to that observed in other coumarin derivatives (Chinnakali *et al.*, 1998, 1999; Krishna *et al.*, 2003). The bond lengths in the dihydropyran ring (*C*) and cyclohexane ring (*D*) have normal values (Allen *et al.*, 1987). In the coumarin moiety, the pyran ring is planar within 0.056 (2) Å and the dihedral angle between the weighted least-squares planes through the benzene and pyran rings (*A* and *B*) is 3.55 (6)°. The dihydropyran ring adopts a half-chair conformation with asymmetry parameter $\Delta C_2(\text{C}12-\text{C}17)$ equal to 0.004 (1) (Nardelli, 1983). The cyclohexane ring (*D*) adopts a chair conformation and the methyl group is equatorially attached to it. The *C/D* ring junction is *trans*. An intramolecular $\text{C}-\text{H}\cdots\text{O}$ hydrogen bond involving the carbonyl O atom is observed. The dihydropyran ring of the symmetry-related molecule at $(\frac{1}{2} + x, \frac{3}{2} - y, -z)$ is involved in a $\text{C}-\text{H}\cdots\pi$ interaction. In Table 2, Cg denotes the centroid of the pyran ring.

Experimental

To a refluxing solution of 4-hydroxycoumarin (1 mmol) in 10 ml of dry ethanol, citranelal (1 mmol) was added and the reaction mixture

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was refluxed for 4 h. Evaporation of the solvent in a rotary evaporator, followed by flash silica-gel chromatography, yielded the title compound. The compound was recrystallized from methanol/chloroform (1:1) by slow evaporation.

Crystal data

$C_{19}H_{22}O_3$	Mo $K\alpha$ radiation
$M_r = 298.37$	Cell parameters from 6654 reflections
Orthorhombic, $P2_12_12_1$	$\theta = 2.9\text{--}27.6^\circ$
$a = 8.8291(4) \text{ \AA}$	$\mu = 0.08 \text{ mm}^{-1}$
$b = 9.8819(4) \text{ \AA}$	$T = 293(2) \text{ K}$
$c = 18.2053(8) \text{ \AA}$	Block, colourless
$V = 1588.38(12) \text{ \AA}^3$	$0.50 \times 0.16 \times 0.14 \text{ mm}$
$Z = 4$	
$D_x = 1.248 \text{ Mg m}^{-3}$	

Data collection

Siemens SMART CCD area-detector diffractometer	1960 reflections with $I > 2\sigma(I)$
ω scans	$R_{\text{int}} = 0.034$
Absorption correction: none	$\theta_{\text{max}} = 28.3^\circ$
11019 measured reflections	$h = -11 \rightarrow 11$
2247 independent reflections	$k = -12 \rightarrow 13$
	$l = -22 \rightarrow 24$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0647P)^2 + 0.1224P]$
$R[F^2 > 2\sigma(F^2)] = 0.042$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.114$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.09$	$\Delta\rho_{\text{max}} = 0.21 \text{ e \AA}^{-3}$
2247 reflections	$\Delta\rho_{\text{min}} = -0.21 \text{ e \AA}^{-3}$
199 parameters	
H-atom parameters constrained	

Table 1

Selected geometric parameters (\AA , $^\circ$).

O1—C9	1.375 (2)	C5—C6	1.377 (3)
O1—C2	1.392 (2)	C5—C10	1.397 (3)
C2—O22	1.200 (2)	C6—C7	1.387 (3)
C2—C3	1.454 (3)	C7—C8	1.380 (3)
C3—C4	1.358 (3)	C8—C9	1.385 (3)
C3—C18	1.512 (3)	C9—C10	1.391 (3)
C4—O11	1.340 (2)	O11—C12	1.474 (2)
C4—C10	1.452 (3)		
O22—C2—O1	115.51 (17)	O1—C9—C8	117.71 (17)
O22—C2—C3	126.39 (19)	C5—C10—C4	123.80 (17)

Table 2

Hydrogen-bonding geometry (\AA , $^\circ$).

$D\text{—}H\cdots A$	$D\text{—}H$	$H\cdots A$	$D\cdots A$	$D\text{—}H\cdots A$
C16—H16B \cdots O22	0.97	2.42	3.061 (3)	123
C19—H19A \cdots Cg ⁱ	0.96	2.90	3.681 (3)	140

Symmetry code: (i) $\frac{1}{2} + x, \frac{3}{2} - y, -z$.

H atoms were positioned geometrically and were treated as riding on their parent C atoms, with aromatic C—H distances of 0.93 \AA , methyl C—H distances of 0.96 \AA , methylene C—H distances of 0.98 \AA and ethylene C—H distances of 0.97 \AA . Due to the lack of anomalous scatterers, the absolute configuration was not determined

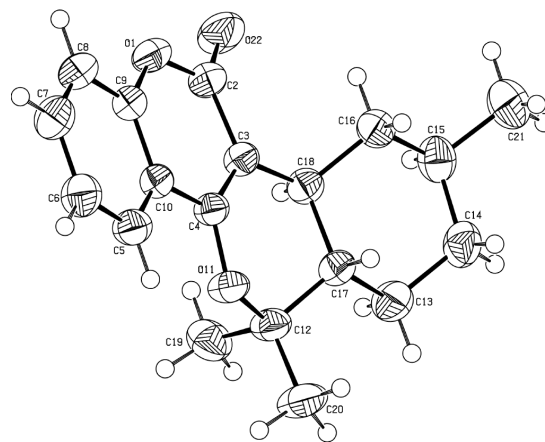


Figure 1

The molecular structure of the title compound, showing 50% probability displacement ellipsoids and the atom-numbering scheme.

from the X-ray diffraction data and the Friedel pairs were merged. The absolute configuration is unknown.

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1996); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *PLATON* (Spek, 1990); software used to prepare material for publication: *SHELXL97* and *PARST* (Nardelli, 1995).

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